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ELECTRON IMPACT STUDY OF NITROGEN

Edwin N. Lassettre and Frederic M. Glaser
Department of Chemistry

December 1962

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ELECTRON IMPACT STUDY OF NITROGEN

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The Ohio State University
Research Foundation
Columbus 12, Ohio

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ABSTRACT

The present study is a reinvestigation of the electron impact spectrum of nitrogen. Electron impact spectra of nitrogen are reported at accelerating voltages of 150, 200, 300, and 400 volts. Since the resolution of the spectrometer is greater than in previous studies, more detailed structure is observed in the spectra and several of the peaks are correlated with bands observed in the vacuum ultraviolet absorption spectrum. A simple method of determining oscillator strengths is used to obtain the oscillator strengths for three prominent peaks. The results are compared with the previous determination.

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ELECTRON IMPACT STUDY OF NITROGEN

I. INTRODUCTION

The electron impact spectrum of nitrogen has been studied in this laboratory previously, (1) to (4), using an electron spectrometer of lower resolving power than that used in the present investigation. The information obtained from these studies was of such a nature that the generalized oscillator strengths of several peaks could be reliably determined and the spectra obtained correlated with optical data in a rather general manner. The assignment of the transitions observed in the electron impact spectra to specific electronic transitions could not be done reliably. Although Krasnow^{1,2} showed that the peak found at 9.2 volts was due to excitation of the forbidden Lyman-Birge-Hopfield band system, the other excitations observed in the impact spectra could not be assigned due to the lack of resolution. Thus, many of the observed peaks were due to excitations to several close-lying states.

The present study is a reinvestigation of the electron impact spectrum of nitrogen using higher resolution than previously. With this improved resolution many broad peaks found prior to this study have been resolved into excitations to a few close-lying states. By determining the position of these peaks on an energy scale accurately by a direct comparison with helium, many of these peaks are found to correlate with the optically observed transitions.

II. THE CALIBRATION OF THE KNUDSEN GAUGE

In the investigation of electron scattering by various gases, it is essential to know the pressure of the gas in the collision chamber. The gas pressure in the collision chamber is measured by noting the deflection of the Knudsen gauge and from this deflection the pressure can be obtained from the calibration constants. Previously, the pressure was obtained by using the calibration constants reported by Lassettre, Silverman, Berman, and Krasnow³ and John⁴. The present recalibration of the Knudsen gauge was prompted by the fact that, when the index of refraction minus one ($n-1$) of oxygen, nitrogen and water are calculated from electron scattering data and are compared with those obtained from optical data, it is found that the discrepancy is about 25 per cent. The index of refraction obtained from electron scattering experiments is greater than that obtained from optical data for each gas. Various possible sources of the discrepancy have been investigated previously. The recalibration of the Knudsen gauge thus forms a portion of this investigation. When the Knudsen gauge was calibrated by Lassettre et al.⁵, a static system was used. In this research the pressure of the gas in the collision chamber was determined under

dynamic conditions. These conditions duplicated those in the electron spectrometer when it was actually in operation except that there was no voltage applied to the parallel plate analyzer or the electron multiplier and no electron beam was directed into the collision chamber.

The Knudsen gauge used was constructed by Distillation Products Inc., Type BL-1. The theory and construction of such a gauge is given by DuMond and Pickels⁷. They derive an equation relating the deflection of the gauge to the pressure, namely,

$$1/D = S/P + C$$

where D is the deflection of the gauge in cm, P is the pressure of the gas in mm Hg, and S and C are parameters characteristic of the Knudsen gauge. The Knudsen gauge is connected to the bottom of the collision chamber by means of a one inch (I.D.) copper tube. Further, the gauge could be thermostated at a temperature of $36 \pm 1^\circ\text{C}$, since the deflection had been found to be dependent upon the prevailing external temperature. The heaters in the gauge were operated at a heating current of 40 milliamperes, since this gives a sensitive response to pressures in the range of 10^{-3} to 10^{-4} mm Hg.

The McLeod gauge used was purchased from the Eck and Krebs Company. This McLeod gauge was equipped with capillaries in which the bore of the tubing had been etched. Rosenberg⁸ has reported that, when capillary tubing with an etched bore was used for constructing thermometers and McLeod gauges, there was little tendency for the mercury to stick and, consequently, give incorrect readings. With the McLeod gauge used in this investigation, no tendency for the mercury to stick could be found and the difference between the heights of the mercury columns could be reproduced to within 0.5 mm. The McLeod gauge was connected to the bottom of the collision chamber through a cold trap and a valve was provided so that the gauge and cold trap could be isolated from the collision chamber. The McLeod gauge was provided with a scale which had been calibrated by the manufacturer so that the gauge could be operated in the linear mode. A check of this scale was made and the capillary examined for uniformity and size by utilizing a traveling microscope. It was found that the scale was correct to about one per cent and no correction was applied to the measurements.

The procedure consisted of allowing the gas to flow through the collision chamber and the deflection of the Knudsen gauge was read and the corresponding pressure was read by the McLeod gauge. Figure 1 shows a typical plot of $1/D$ vs. $1/P$ for nitrogen which was used to determine the parameters S and C. These same data for nitrogen are plotted as D vs. P in Fig. 2 so that the pressure may be found directly from the deflection.

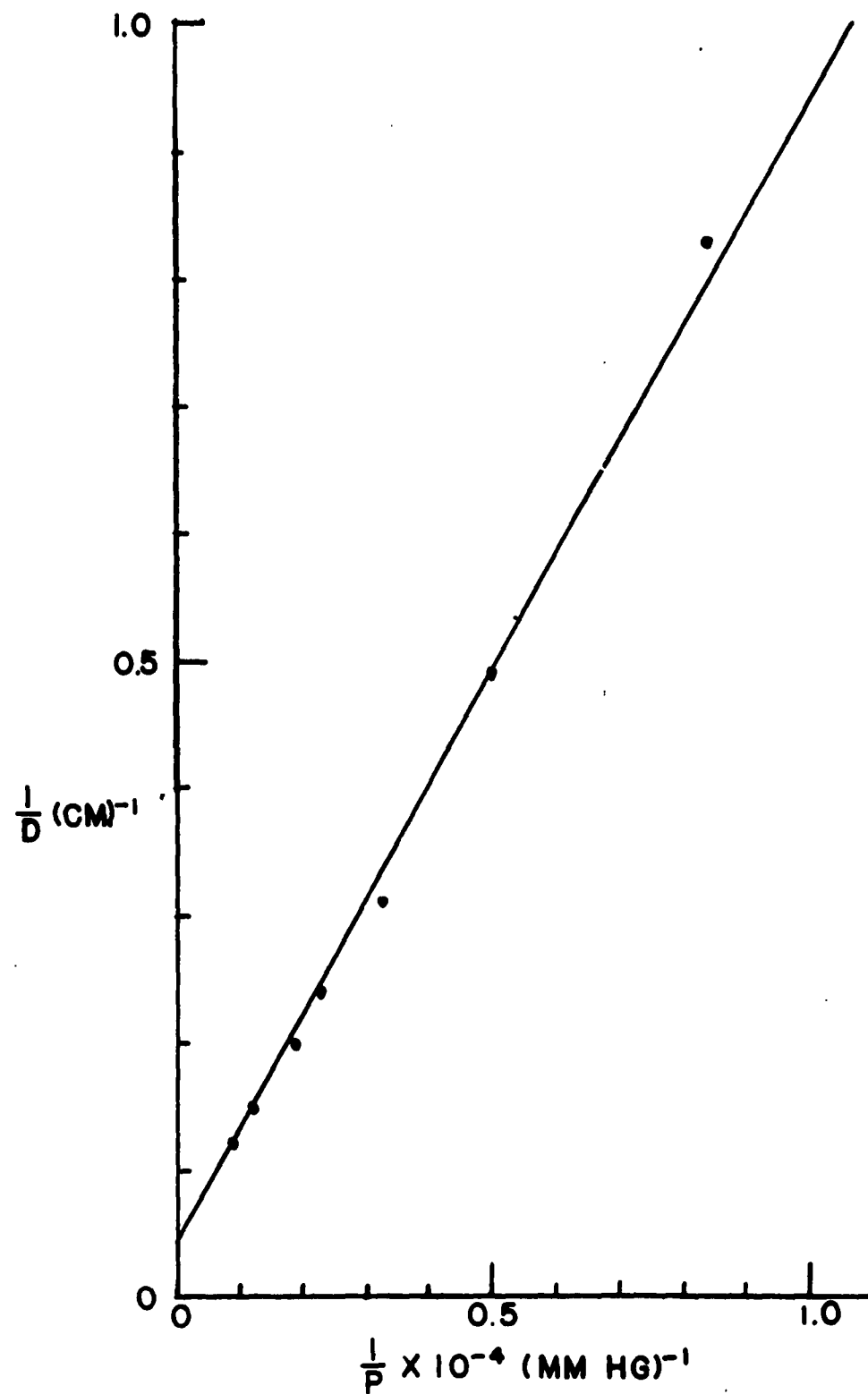


Fig. 1. Calibration of Knudsen Gauge $1/D$ vs. $1/P$

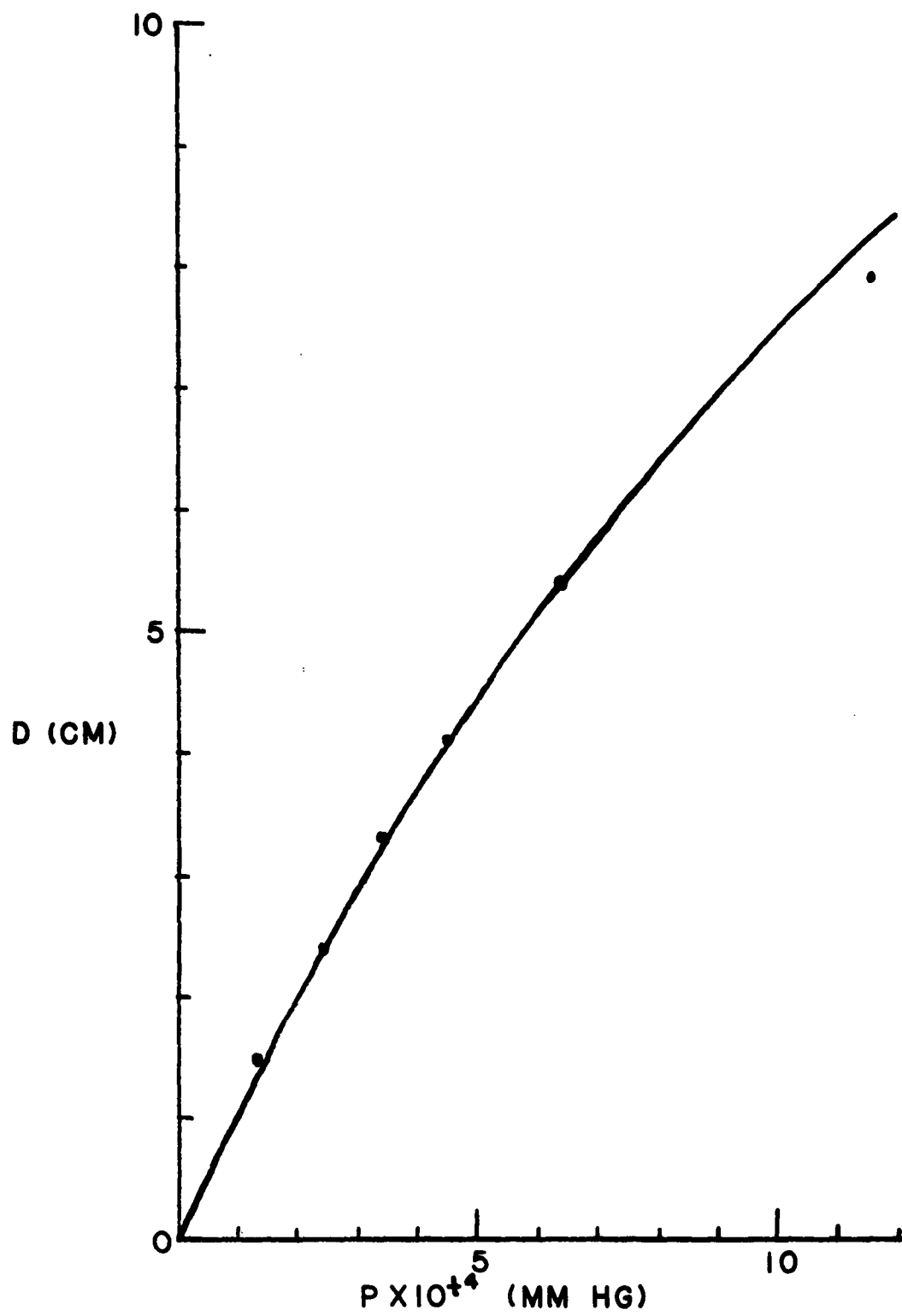


Fig. 2. Calibration of Knudsen Gauge D vs. P

Since the Knudsen gauge has been reported to be independent of the gas, except possibly hydrogen and helium, three gases were used for calibration purposes: helium, nitrogen, and carbon dioxide. The calibration studies were also carried out at room temperature ($27 \pm 1^\circ\text{C}$) and $36 \pm 1^\circ\text{C}$. In correlating the data, the method of least squares was used for each determination and for all the measurements made with each gas at a particular temperature. The slopes and intercepts, determined by the least-squares treatment of all the data for each gas and temperature, are recorded in Table 1. The number of determinations is also shown in this table. The last row in this table at each temperature are the values of the slope and intercept obtained when the data for each gas are treated together.

The probable error in the pressure was determined by calculating the pressure using the slope and intercept as determined by each calibrating run. The average value of the pressure and probable error, p , are shown in Table 2 for each gas and temperature. The pressure and probable error were calculated for two deflections of the Knudsen gauge most commonly used, 5 cm and 3 cm.

Table 1. Calibration Constants for Knudsen Gauge

Gas	Number of Runs	Slope $\times 10^5$	Intercept
$27 \pm 1^\circ\text{C}$			
He	4	9.717	0.04638
CO ₂	4	8.891	0.04287
N ₂	4	9.029	0.04685
average		9.509	0.03250
$36 \pm 1^\circ\text{C}$			
He	5	10.017	0.05160
CO ₂	2	9.397	0.03665
N ₂	3	8.634	0.05173
average		9.466	0.04900

Table 2. Gas Pressure in Collision Chamber
at 5 cm and 3 cm Deflections

Gas	5 cm Deflection	p	3 cm Deflection	p
	P x 10 ⁴ mm Hg.		P x 10 ⁴ mm Hg.	
27 ± 1°C				
He	6.35	0.17	3.41	0.05
N ₂	5.90	0.26	3.15	0.04
CO ₂	5.61	0.16	3.06	0.06
36 ± 1°C				
He	6.89	0.25	3.64	0.05
N ₂	5.81	0.06	3.08	0.03
CO ₂	5.75	0.08	3.16	0.04

From this table it can be seen that the error in the average pressure for each gas is about four per cent at most. Further, the Knudsen gauge is not entirely independent of the gas, although the pressures of nitrogen and carbon dioxide are equal to within the probable error at each deflection and temperature. However, at each temperature and deflection the helium pressure is greater than the corresponding nitrogen and carbon dioxide pressure and the difference is greater than the probable errors. This effect presumably persists over the range of deflections of interest and indicates that the Knudsen gauge is not independent of the gas, although the difference between helium and nitrogen is less at the lower temperature. This difference is about 9 per cent at 27°C and 15 per cent at 36°C.

A direct comparison with the calibration data obtained by Lassetre, et al.⁵ is not possible because the suspension of the Knudsen gauge had been changed since that calibration was made. However, it should be noted that Lassetre, et al. concluded that this same gauge was independent of the gas to within an experimental error of about four per cent. The source of the difference between helium and nitrogen and carbon dioxide was not investigated but it could arise from a difference in the accommodation coefficient or perhaps from the fact that the Knudsen gauge was recalibrated using a dynamic system.

When the measurements were made, the gas was introduced into the collision chamber from either of two valve systems. The two valve systems were designed to be independent of each other so that electron scattering

by gas mixtures could be investigated. It was convenient to investigate possible sources of error in the pressure measurements caused by differences in these valve systems. It will be convenient to label these valve systems as right and left. The slope and intercept for each gas and temperature are shown in Table 3 together with the number of runs made using valve system right and left. Again the least squares method was used to treat each group of data.

Table 3. Calibration Constants for Knudsen Gauge
Using Right and Left Valve Systems

Gas	Number of Runs	Slope $\times 10^5$	Intercept
$27 \pm 1^\circ\text{C}$			
He (right)	2	10.042	0.03979
(left)	2	9.492	0.05035
N ₂ (right)	2	8.695	0.05088
(left)	2	9.478	0.03995
CO ₂ (right)	2	9.196	0.03882
(left)	2	8.733	0.04483
$36 \pm 1^\circ\text{C}$			
He (right)	2	10.046	0.04981
(left)	3	9.996	0.05282
N ₂ (right)	2	8.777	0.04768
(left)	1	8.489	0.05664
CO ₂ (right)	1	9.448	0.03073
(left)	1	9.351	0.04233

The probable error in the pressure was determined as before and the pressure and the mean deviation, d , for each gas using valve system right and left are recorded in Table 4. Again the pressures are calculated for the two most commonly used deflections, 5 cm and 3 cm.

Table 4. Gas Pressure in Collision Chamber
Using Right and Left Valve Systems

Gas	5 cm Deflection $P \times 10^4$ mm Hg	d	3 cm Deflection $P \times 10^4$ mm Hg	d
$27 \pm 1^\circ\text{C}$				
He (right)	6.33	0.30	3.37	0.19
(left)	6.37	0.20	3.55	0.05
N ₂ (right)	5.86	0.46	3.07	0.08
(left)	5.93	0.30	3.23	0.07
CO ₂ (right)	5.60	0.34	3.10	0.14
(left)	5.62	0.02	3.02	0.06
$36 \pm 1^\circ\text{C}$				
He (right)	6.64	0.11	3.55	0.03
(left)	7.05	0.29	3.71	0.17
N ₂ (right)	5.75	0.07	3.08	0.04
(left)	5.92	0.10	3.07	0.02

An examination of this table shows that the pressures determined at each deflection agree rather well using the left and right valve systems. In every case the pressures agree to within the estimated error. Thus, the Knudsen gauge is independent of the valve system used to regulate the gas flow into the collision chamber. This is important since the electron impact spectrum of a helium-nitrogen mixture was determined and the individual gases were introduced into the collision chamber using this valve arrangement.

III. EXCITATION POTENTIALS OF NITROGEN

The determination of the excitation potentials of nitrogen has been reported in detail in an earlier report. The procedure and results will be outlined only briefly here. The excitation potential of the most intense transition in the nitrogen spectrum was determined in two ways. The impact spectrum of a helium-nitrogen mixture was obtained using accelerating voltages of 400 and 500 volts. Since the 1'S-2'P transition in helium is known to occur at 21.21 volts, the excitation potential of the most intense peak in nitrogen could be found from the voltage separation, V. It has been shown and reported that the voltage divider reading, V, is

related to the kinetic energy of the electrons passing through the analyzer by the linear relation $T = KV$ where $K = 1.019$. Hence, the excitation potential of the nitrogen peak is given by $E = 21.21-KV$. The average value of E and the mean deviation found from 13 determinations was $E = 12.91 \pm$

When the impact spectrum of nitrogen was examined in the range of 17 to 19 volts, four peaks were found which were assigned to the first five members of Hopfield's Rydberg series. The fourth and fifth members were unresolved and correspond to the fourth peak observed in the impact spectrum. The voltage divider readings of these four peaks were used together with the optical excitation potentials to locate the most intense nitrogen peak. The average value of the excitation potential of the most intense nitrogen peak which best fit these optical data was found to be 12.94 ± 0.1 volts.

By comparing the excitation potentials obtained from fitting the optical data and that obtained from the helium-nitrogen mixture spectra the most probable value was taken to be $12.93 \pm .03$ volts. Having accurately determined the excitation potential of the most intense transition in nitrogen, this peak is used to locate the other peaks relative to 12.93 volts.

IV. NITROGEN SPECTRUM

The nitrogen spectra which are shown in Figs. 3 to 7 were obtained using accelerating voltages of 400, 300, 200, and 150 volts. These spectra were obtained in the usual manner. It should be pointed out, however, that the spectrum obtained using an accelerating voltage of 150 volts was determined by scanning only portions of the energy loss range and that Fig. 7 is a composite of these portions. The reason for scanning only portions at a time is that due to the low intensity, the spectrometer was not sufficiently stable for the three hours required to scan the entire region. For this reason this spectrum is considered to be less reliable than the others which were scanned over the entire region in one operation.

The peaks for the energy loss range 12 to 19 volts are listed in Tables 5 and 6. Also, the peaks observed by Silverman³, Krasnow^{1,2}, and Skerbele⁴ are listed in these tables for reference. It should be noted that 0.08 volt has been added to each of these workers' values since the most intense peak in the nitrogen spectrum had been determined to occur at 12.85 volts and the other peaks were determined relative to this peak. In the present investigation this peak was determined to occur at 12.93 volts; hence, the change of scale. In addition, Skerbele's have been corrected by employing the instrument constant ($K = 1.019$) as outlined in the previous section. The excitation potentials in Table 5 should be correct to within ± 0.08 volt. Since the most intense transition at

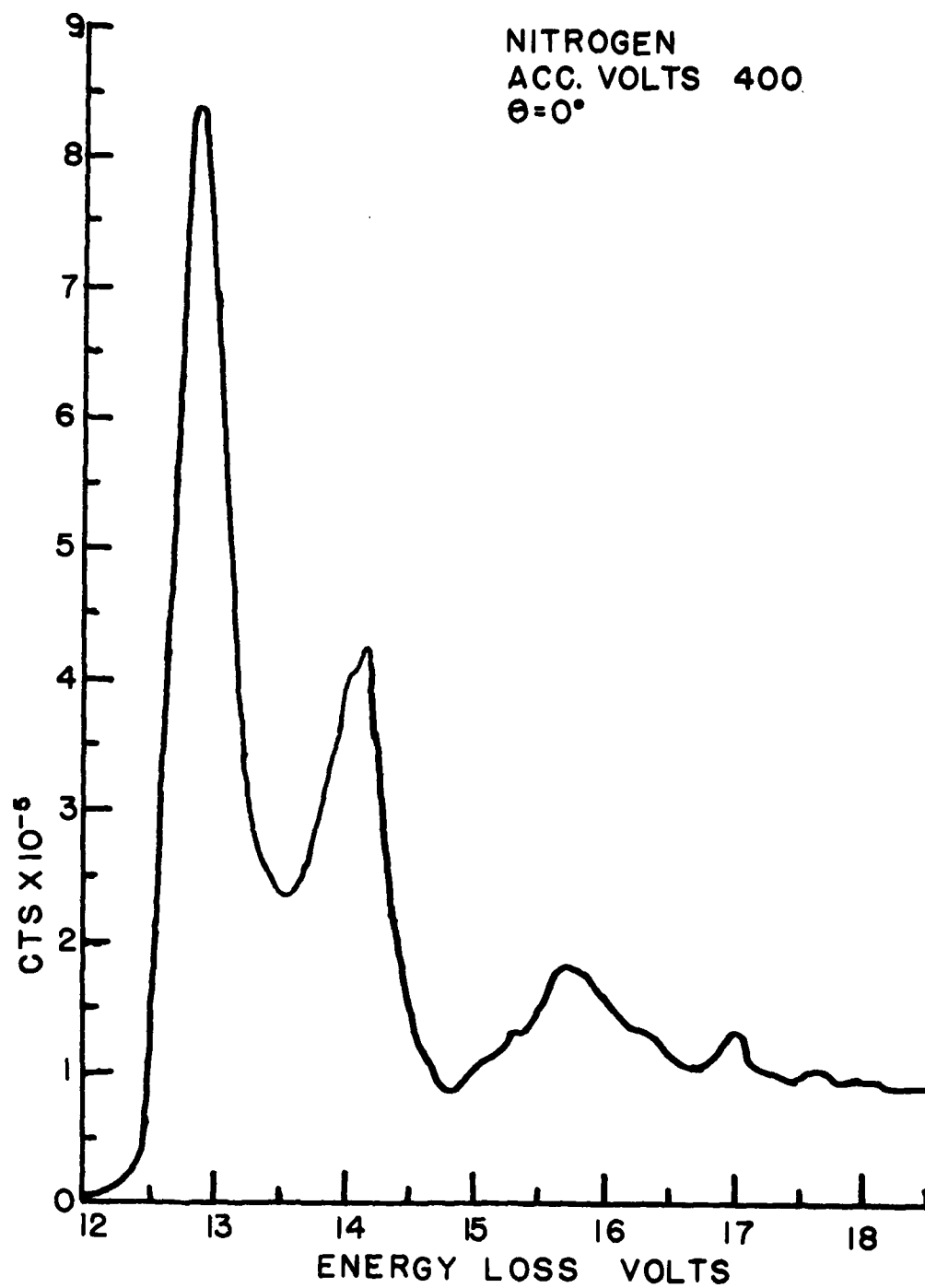


Fig. 3. Nitrogen Spectrum using 400 Volts

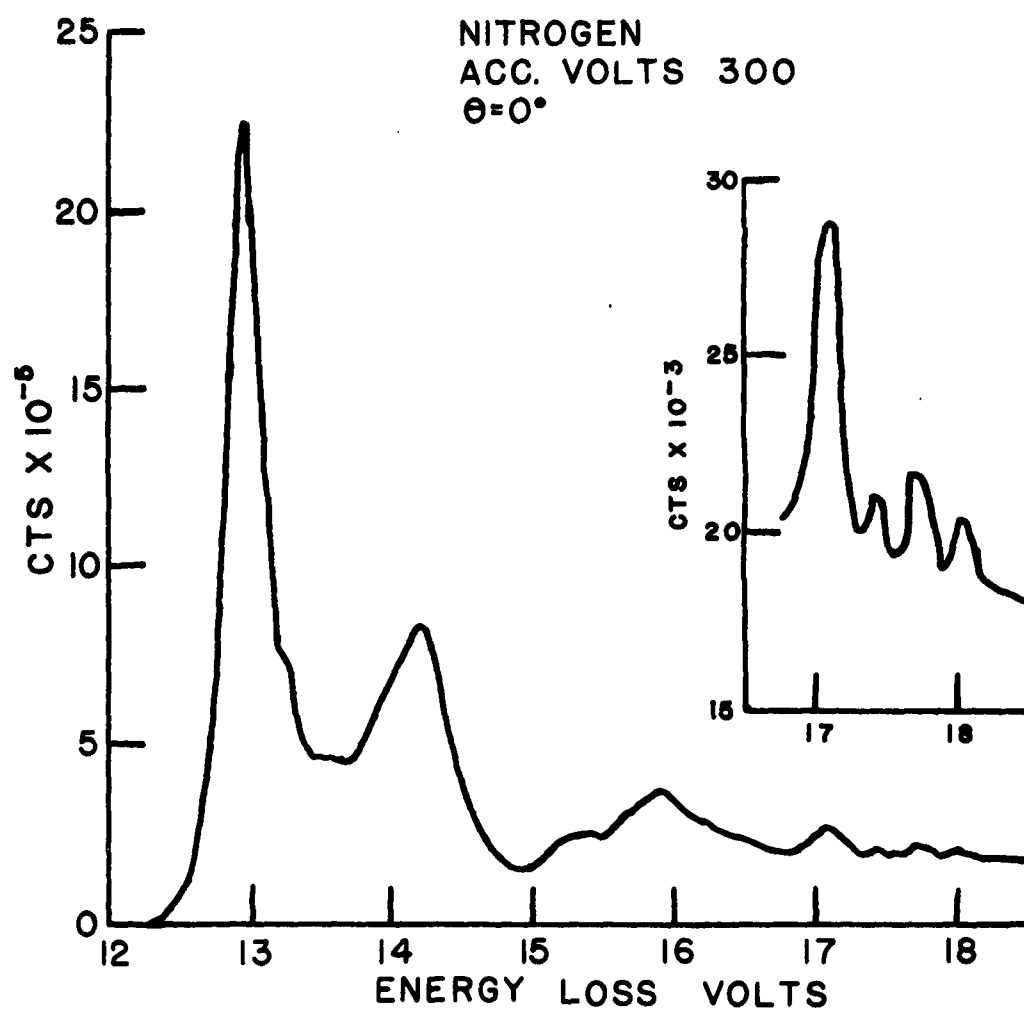


Fig. 4. Nitrogen Spectrum using 300 Volts

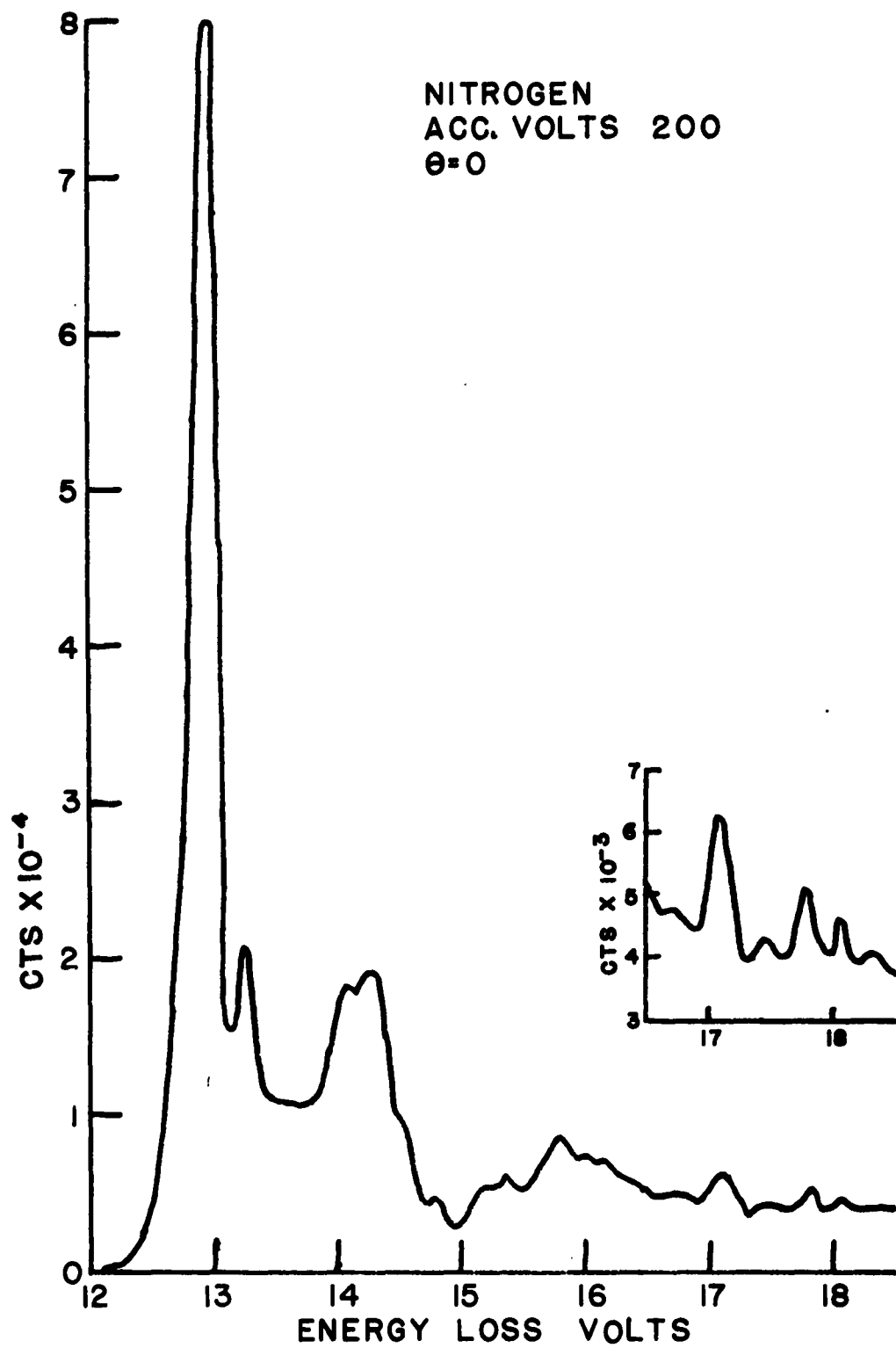


Fig. 5. Nitrogen Spectrum using 200 Volts

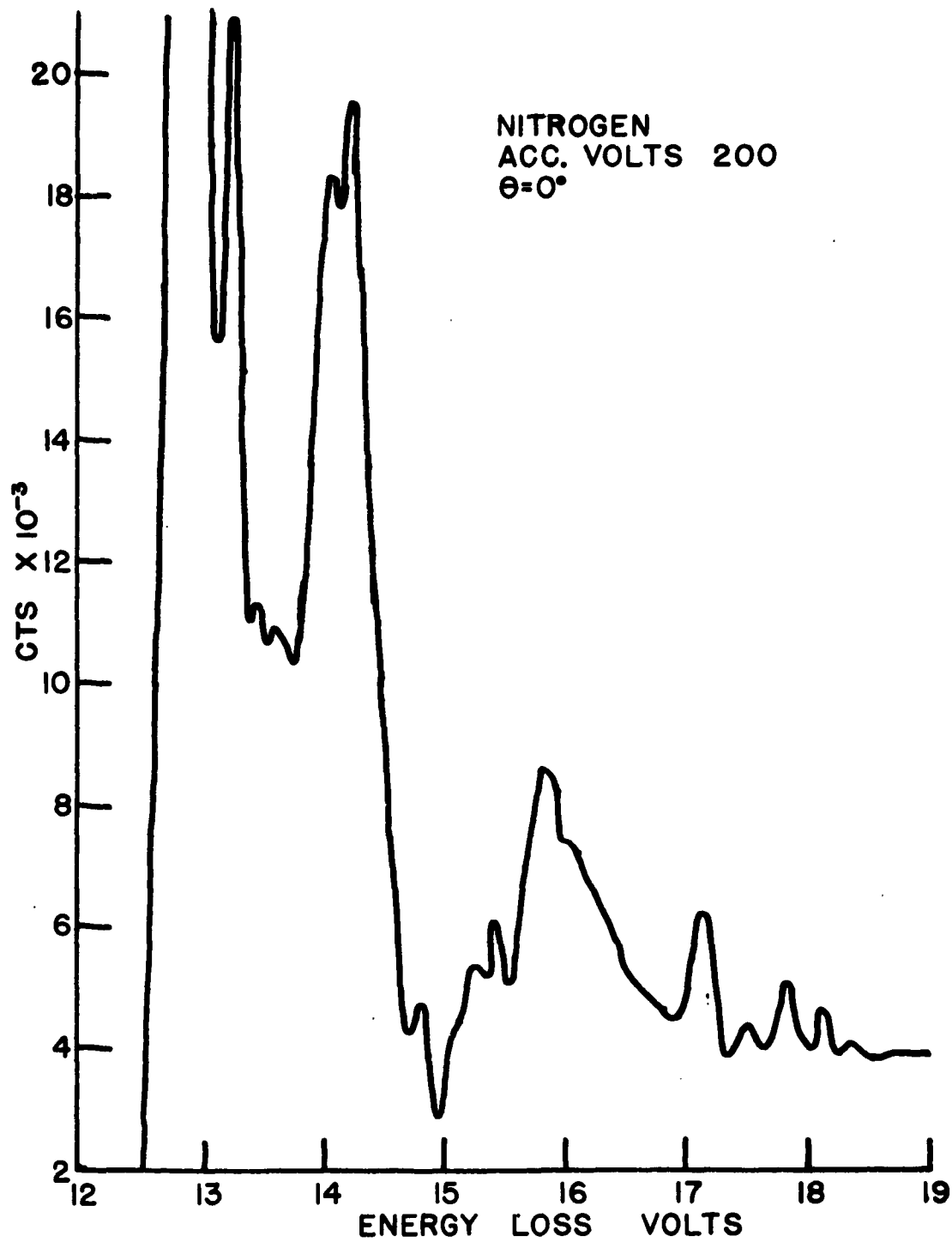


Fig. 6. Nitrogen Spectrum using 200 Volts

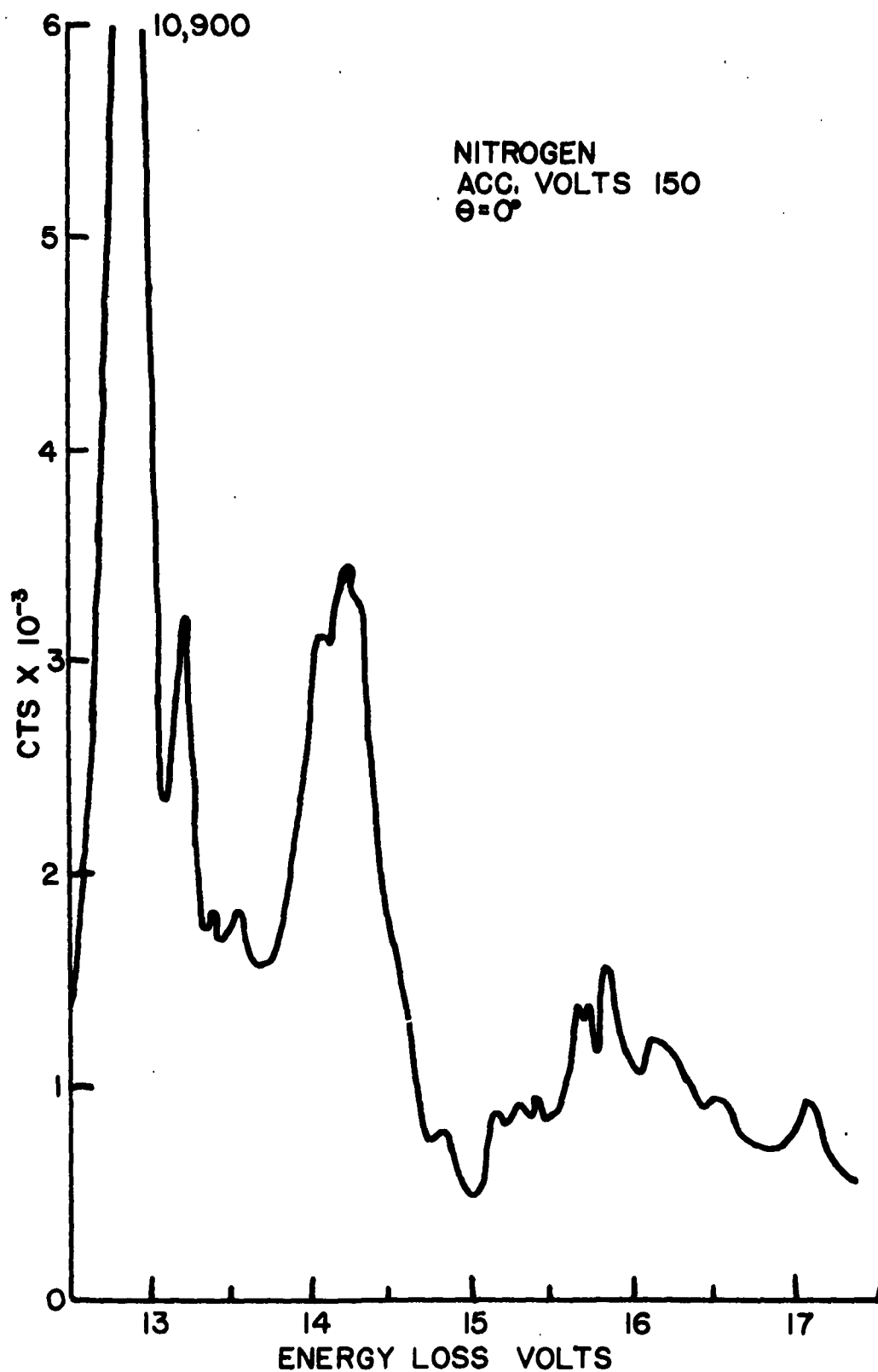


Fig. 7. Nitrogen Spectrum using 150 Volts

12.93 volts is correct to within ± 0.03 volt and since the spectrum was scanned using 0.025-volt intervals, an error not exceeding ± 0.08 volt seems reasonable. The peaks listed in Table 5 are those which were reliably determined. That is, they appear in the 150-volt spectra as well as those taken at higher accelerating voltages. There can be little doubt that these peaks are real since they were observed repeatedly in 200-volt spectra. The positions reported in Table 6 are less reliable since they were observed only in 150-volt spectra which are the least reliable reported here.

Table 5. Peak Positions of the Nitrogen Spectrum
in the Range 12 to 19 Volts

This Investigation	Skerbele	Krasnow	Silverman
12.93	12.93	12.93	12.93
13.22			
13.42			
13.58			
14.10	14.12	14.09	14.07
14.28			
14.85			
15.75			
15.89	15.89	16.00	15.97
17.12	17.16	17.31	17.33
17.52			
17.82	17.77		
18.14			
18.43			

Table 6. Additional Peaks in the Nitrogen Spectrum
in the Range 12 to 19 Volts

This Investigation	Skerbele
15.15	
15.32	
15.47	
16.25	
16.59	16.50

It is seen from these tables that a considerable number of new peaks has been located. Most of these new peaks occur in the region near 14 volts and 15 to 16 volts where rather broad absorption peaks had been found prior to this research. With the increased resolution it was, indeed, expected that these broad peaks would be resolved. However, even with the increased resolution, many of the peaks found in the present investigation are due to a combination of transitions. The most noteworthy example is the most intense peak in the spectrum at 12.93 volts.

In Table 7 the peaks found in the nitrogen spectrum in the range 12 to 19 volts are compared with those bands reported by Worley¹¹. From the data given by Worley those bands reported to have a relative intensity of one or greater (based on 15 for the most intense band) were listed and the peaks observed in this investigation were compared with this list. The results of this comparison form Table 7. The relative intensities are also given as reported by Worley and determined in this investigation. The relative intensity was obtained by calculating the ratio of the counting rate at the peak in question to the counting rate of the most intense transition. The most intense transition at 12.93 volts was then assigned the relative intensity 15 and the other peaks scaled accordingly. It should be pointed out again that, although only one band from Worley's data has been taken to make this comparison, there are in reality several close-lying bands of lesser intensity in most cases. This, of course, introduces an additional uncertainty into the assignment of observed peaks.

As can be seen from this table, good agreement can be obtained with the optical data with respect to the position of the peaks. Meyer¹⁰ also found that the excitation potentials determined from the impact spectrum of carbon dioxide agree well with optically determined values. However, the intensity data obtained in the present investigation do not agree very well in most cases. In the last column of this table the peaks have been identified with certain electronic states as indicated by Worley¹¹, Herzberg¹², Takamine¹³, and Tanaka¹⁴. In general, the notation for the various term symbols is that used by Herzberg¹². In addition, $R_0(m)$, $m = 2, 3, \dots 26$ signify the terms of the Worley-Jenkins (0,0) Rydberg series. $R_1(m)$, $m = 2, 3, \dots 17$ signifies the terms of the Worley-Jenkins (1,0) Rydberg series; and finally, $R_3(m)$, $m = 3, 4, \dots 10$ signifies Hopfield's Rydberg series. The vibrational level assignments of $v' = 13, 14, 15, 16$ for the $r^1\Sigma_u^+$ state are taken from the paper presented by Ogawa and Tanaka¹⁵. The assignment of these peaks in the impact spectrum is discussed more fully by Glaser¹⁶.

Finally, a short discussion of the resolution and stability of the electron spectrometer is of interest. Prior to scanning the impact spectrum of nitrogen, the most intense peak was scanned several times in order to ascertain the stability and resolution of the spectrometer. The stability is indicated by the consistency with which the maximum of the 12.93 peak is reproduced on the voltage divider scale. Most erratic behavior or drift in the spectrometer can be detected by noting any shift in peak position, intensity, or peak half-width. Table 8 shows the results of these measurements which were obtained by scanning the 12.93 volt peak using 0.025-volt intervals and an accelerating voltage of 150 volts. In each group the measurements were made consecutively.

Table 7. Comparison of the Observed Excitation Potentials
in the Nitrogen Spectrum with Optical Data

This Investigation		Optical		Assignment
Volts	Intensity	Volts	Intensity	
12.93	15	12.93	3	$p'^1\Sigma_u^+ (v' = 0), R_0(2)$
13.22	4	13.21	8	$p'^1\Sigma_u^+ (v' = 1)$
13.42	2	13.35	6	$o^1\Sigma_u^- (v' = 0)$
13.58	2	13.58	5	$o^1\Pi_u (v' = 1)$
14.10	4	14.08	4	$r^1\Sigma_u^+ (v' = 13, 14)$
14.28	4	14.32	3	$e^1\Sigma_u^+, R_0(3)$
14.85	1	14.81	3	$R_0(4)$
15.15	1	15.14	4	$R_0(5), R_1(5)$
15.32	1	15.37	5	
15.47	1	15.47	1	
15.75	2	15.70	5	
15.89	2	15.88	3	
16.25	2	16.30	5	
16.59	1	16.67	3	
17.12	2	17.13	2	$R_3(3)$
17.52	2			
17.82	1	17.84	3	$R_3(4)$
18.14	1	18.17	2	$R_3(5)$
18.43	1	18.41 (ave.)	2	$R_3(6), R_3(7)$

Table 8. Stability and Resolution of the Spectrometer on Various Days

Date	Position (Voltage Divider Reading)	Half-Width	Intensity CTS x 10 ⁻³
6/4/62	713	0.280	8.2
	715	0.280	7.8
	714	0.285	7.7
6/13/62	732	0.230	18.0
	730	0.242	17.0
	731	0.230	15.5
	730	0.230	16.0
6/14/62	720	0.240	2.6
	719	0.234	3.8
	723	0.245	2.4
6/18/62	723	0.229	10.1
	724	0.229	11.0

When half-widths such as those shown in the first group of data were encountered, any spectra obtained that day were disregarded since this peak was very broad and indicates poor resolution. Operations were temporarily discontinued and the cathode and heater replaced and the hemispherical analyzer cleaned. The effect of changing the cathode and heater and cleaning the hemisphere electrodes and slit assemblies is shown rather strikingly by the other three groups of data. Further, the stability of the spectrometer is indicated by the voltage divider readings found for the peak maximum. It can be seen that in each group the spectrometer had reached a steady operating state when the peak was scanned but the peak position changed by a significant amount from day to day. On occasion the peak position would shift by as much as 0.20 volt while making these preliminary observations. This shift in peak position indicated that the cathode was still activating and by allowing it to continue to activate stable operations could usually be achieved. The desirability of scanning this nitrogen peak prior to scanning the entire spectrum is obvious.

V. CROSS SECTIONS OF NITROGEN

The procedure heretofore used for the determination of electronic collision cross sections involved a preliminary calibration of the apparatus with helium, followed by an angular scattering study of some prominent peak in the spectrum of the gas under study, and a final calibration with helium to ensure that no change in the apparatus constant had taken place. A difference in the apparatus constant with a change in gas may arise because of changes in accelerating voltage, emitter activity, or drift of the analyzer voltage. A method which eliminates these factors involves a study of the scattering by a mixture of helium and nitrogen. Any changes can be detected and corrected quickly since only narrow energy loss ranges about the 21.21-volt peak of helium and the 12.93-volt peak of nitrogen are scanned.

In the previous studies a scattering angle in excess of four degrees was used in order to eliminate the problem of beam divergence encountered at zero scattering angle. Since that time a hemispherical velocity selector, providing velocity selection before scattering, has been incorporated into the apparatus. This reduced the beam current to such an extent that at scattering angles of four or more degrees the intensity of the scattered beam was not sufficient to study even the most intense transitions. However, velocity selection before scattering has reduced the beam divergence and Skerbele⁴ demonstrated that it is possible to determine oscillator strengths at zero scattering angle for several of the most intense transitions in the helium spectrum. She first assigned the value of 0.286 a.u. for the oscillator strength of the 1'S-2'P transition and then calculated the oscillator strengths for the 1'S-n'P, n = 3, 4, 5 transitions from the intensity ratios and this assigned oscillator strength. In order to calculate these oscillator strengths in this manner, she assumed that the peak envelopes were all the same. The oscillator strengths determined in this manner were in good agreement with those found by other methods. This suggests that it may be possible to determine oscillator strengths in molecular spectra at zero scattering angle by using the helium-molecular gas mixture method. However, since the uncertainty in scattering angle cannot be completely eliminated, it may be necessary to make some correction for it.

The equations required to obtain the generalized oscillator strength are presented and explained below. The derivation of these relationships has been given by Lassette¹⁷.

The collision cross section, S, for an unresolved transition such as the 12.93-volt peak, is given by,

$$S = \frac{K_e \alpha_p \ell I_m}{pV(E-W)I_0} \quad (1)$$

where

K = an apparatus constant

α = total absorption coefficient

ℓ = path length of the electron beam

p = pressure of gas in collision chamber

V = scattering volume

E = incident electron energy

W = energy loss of the electron on collision

I_m = maximum scattered current for the transition under study

I_0 = beam current

A similar equation holds for the cross section for a well-resolved transition, such as the 21.21-volt helium peak. Thus, the cross section, σ , is

$$\sigma = \frac{K b e^{\alpha p \ell} I_m}{p V (E - W) I_0} \quad (2)$$

where the symbols have the same meaning as before and $b = 1/I_m \int I dW$ = ratio of area to height for the transition being studied. Here, I , is the scattered current for a given energy loss W . The relation between electronic collision cross sections and optical oscillator strength is given by

$$\lim_{(\Delta P)^2 \rightarrow 0} f = f^0 \quad (3)$$

Here f is the generalized oscillator strength, f^0 the optical oscillator strength, and $(\Delta P)^2$ is the square of the colliding electron's momentum change. The generalized oscillator strength f for an unresolved transition

is related to the cross section by

$$f = \frac{W}{2} (\Delta P)^2 \frac{P}{P'} bS \quad (4)$$

where P and P' are the incident electron and scattered electron momenta respectively. A similar expression holds for a well resolved transition in which bS is replaced by σ .

These equations have been derived by considering a perfectly collimated incident electron beam. Meyer¹⁰ has shown that these results should be corrected for the uncertainty in scattering angle and has given the relation

$$\bar{\sigma} = \left[1 + F(\eta) \right] \sigma \quad (5)$$

where $\bar{\sigma}$ is the measured cross section and

$$F(\eta) = 0.01153 \left[(1/\eta + \eta \times 10^5 / 8.752) \tan^{-1}(9.355 \times 10^{-3} / \eta) - 43.37 \right. \\ \left. - (1/\eta + \eta \times 10^4 / 2.477) \tan^{-1}(1.574 \times 10^{-2} / \eta) \right] \quad (6)$$

where $\eta = W/(2E-W)$. In the case of nitrogen this correction for the scattering angle uncertainty is approximately ten per cent. A similar expression holds for S.

In this section the assumption is made that at 27°C the Knudsen gauge is nearly independent of the gas so that the pressure of the helium-nitrogen mixture can be calculated using the average values of the gauge constants. The error introduced into the generalized oscillator strength by this assumption will be investigated at the end of this section. Making this assumption then, the ratio of the generalized oscillator strengths is

$$\frac{f_2}{f_1} = \frac{W_2 (\Delta P_2)^2 P_1' P_2 (E-W_1) b_2 I_{m_2} [1 + F(\eta_1)]}{W_1 (\Delta P_1)^2 P_1 P_2' (E-W_2) b_1 I_{m_1} [1 + F(\eta_2)]} \quad (7)$$

where the subscripts 1 and 2 refer to the values of the parameters of helium and nitrogen respectively. Since all the quantities on the right hand side of this equation are found from experiment and f_1 is known from theory, f_2 , the generalized oscillator strength for the 12.93 volt nitrogen peak, can be calculated. The value of f_1 used in the calculations should be the value at $(\Delta P_1)^2 = 1.689 \times 10^{-3}$ atomic units. The error introduced by using the value of f_1 extrapolated to $(\Delta P_1)^2 = 0$ is less than one per cent as can be estimated from the plot of f_1 vs. $(\Delta P_1)^2$ given by Lassetre and Silverman^{3,18}. Further, the value of f_2 calculated from the gas mixture data will be the value at $(\Delta P_2)^2 = 6.202 \times 10^{-3}$ a.u. The error in f_2 due to error in f_1 , the differential oscillator strength, are the same since $f_2 \approx b_2 f_1$ and $b_2 \sim 1$.

The calculation of $(\Delta P)^2$ and b follow from the customary equations $(\Delta P)^2 = 8E [\sin^2 \theta + W^2 / (4E)^2]$ and the b value was calculated by summing the product of the counting rate measurements and energy loss interval. An energy loss interval of 0.05 volt was used in all calculations. Since there is an appreciable amount of scattered current near 21 volts, which is due to excitations to the nitrogen continuum, the counting rate measurements for the 21.21-volt helium peak were corrected by this amount. The b value for the nitrogen peak, b_2 , was calculated in the same manner except now no background correction is made and the high energy side of the peak was extrapolated as a straight line to zero counting rate. Figure 8 shows a typical spectra of the helium-nitrogen mixture run. The oscillator strengths of the 14.10-volt and 15.91-volt peaks can be calculated from an equation of the same form as equation 7. Now the subscript 1 refers to the 12.93-volt nitrogen peak and subscript 2 refers to the peak in question. Equation 7 must be used rather than simply the intensity ratios since the peak envelopes are not the same as was the case for helium investigated by Skerbele⁴. The results obtained from the spectra taken in the present investigation are compared in Table 9 with those reported by Silverman³.

Table 9. Oscillator Strengths for Three Prominent Nitrogen Peaks

Position (volts)	This research	Silverman
12.93	$0.876 \pm .061$	0.872
14.10	$0.641 \pm .034$	0.602
15.91	$0.456 \pm .059$	0.492

HELIUM-NITROGEN MIXTURE
ACC. VOLTS 500
 $\theta=0^\circ$

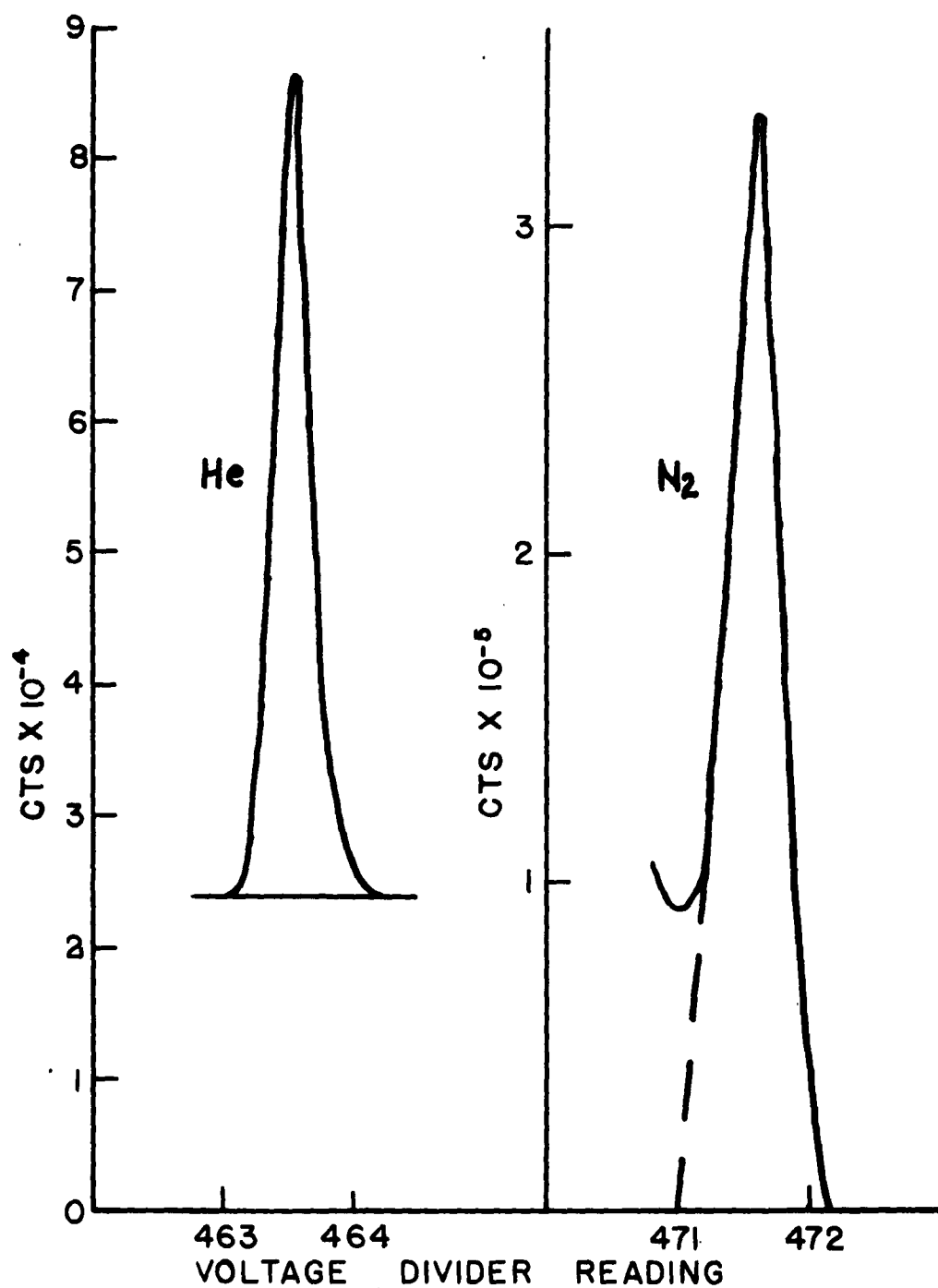


Fig. 8. Helium-Nitrogen Mixture Spectrum

The good agreement of these oscillator strengths and those of Silverman is fortuitous since the internal consistency is only about seven per cent and the correction for the difference of the partial pressures has not been made.

Finally, we wish to investigate the consequences of the assumption made concerning the pressure measurements. Referring back to equation 7, let us rewrite this equation as

$$\frac{f_2}{f_1} = K'' \quad (10)$$

We see that when the partial pressures are not equal equation 10 becomes

$$\frac{f_2}{f_1} = K'' \frac{P_1}{P_2} \quad (11)$$

using equations 1 and 2. Using the values of the slope and intercept for helium and nitrogen given in Table 1 the partial pressures are $p_1 = 2.87 \times 10^{-4}$ mm Hg and $p_2 = 2.67 \times 10^{-4}$ mm Hg. Thus we obtain $f_2 = 0.937 \pm .065$ using equation 11.

From this calculation it is apparent that if the Knudsen gauge is assumed to be independent of the gas than an error of approximately seven per cent is introduced into the calculated generalized oscillator strengths. The corrected oscillator strengths and mean deviations for the three most prominent nitrogen peaks are listed in Table 10.

From this table it can be seen that the results agree quite well, in fact to within about ten per cent. Meyer¹⁰ also found that when the oscillator strengths for carbon dioxide were determined from a helium-carbon dioxide mixture these agreed rather well with previous observations. The relatively large mean deviations found in the present investigation may be due to errors in the b values which are difficult to determine. This is particularly true of the 14.10-volt and 15.91-volt peaks where considerable overlapping with neighboring peaks occurs.

Table 10. Corrected Oscillator Strengths
for Nitrogen

Position Volts	This Research	Silverman
12.93	0.937 ± 0.065	$0.872 \pm .049$
14.10	0.686 ± 0.036	$0.602 \pm .030$
15.93	0.488 ± 0.063	$0.492 \pm .025$

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